



# Spatial and temporal trends in occurrence of emerging and legacy contaminants in the Lower Columbia River 2008–2010

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## HIGHLIGHTS

- SPMDs and POCIS were used to track trends in contaminant concentrations.
- Contaminant profiles were related to surrounding land-use.
- Temporal trends are poorly defined while chemical loadings followed rainfall levels.

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## ABSTRACT

The Lower Columbia River in Oregon and Washington, USA, is an important resource for aquatic and terrestrial organisms, agriculture, and commerce. An 86-mile stretch of the river was sampled over a 3 year period in order to determine the spatial and temporal trends in the occurrence and concentration of water-borne organic contaminants. Sampling occurred at 10 sites along this stretch and at 1 site on the Willamette River using the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) passive samplers. Contaminant profiles followed the predicted trends of lower numbers of detections and associated concentrations in the rural areas to higher numbers and concentrations at the more urbanized sites. Industrial chemicals, plasticizers, and PAHs were present at the highest concentrations. Differences in concentrations between sampling periods were related to the amount of rainfall during the sampling period. In general, water concentrations of wastewater-related contaminants decreased and concentrations of legacy contaminants slightly increased with increasing rainfall amounts.

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## 1. Introduction

The Columbia River provides important hydroelectric power generation, valuable recreational and tribal fisheries, extensive recreational areas and scenic beauty, and habitat for wildlife and fish. The lower Columbia River below Bonneville is the largest remaining free-flowing reach not impounded by hydroelectric dams in the Columbia Basin, and is critical to the viability of culturally significant fish populations (anadromous and resident), as well as a myriad of other aquatic and terrestrial organisms. Fish, wildlife, and human populations along the lower Columbia River are exposed to an ever-growing variety of contaminants as a result of increasing urbanization, industrialization and agricultural development (Nilsen and Morace, 2014—in this issue).

The work presented here is part of the US Geological Survey's (USGS) Columbia River Contaminants and Habitat Characterization (ConHab, <http://or.water.usgs.gov/proj/Conhab/>) joint effort to address

how emerging contaminants, such as polybrominated diphenyl ether flame retardants (PBDEs) and endocrine disrupting compounds (EDCs), impact fish, osprey, and other wildlife in the basin. One of the purposes of the ConHab project is to fill knowledge gaps associated with the occurrence and bioaccumulation of PBDEs and EDCs to improve the ability of management agencies to evaluate the actions that are the most likely to result in improving river and estuarine conditions for salmonids and other organisms. The presence and effects of these emerging contaminants are important issues that have high scientific and public visibility and potentially important implications for people, fish, and wildlife in the Columbia River Basin.

Recent studies (Lower Columbia River Estuary Partnership, 2007; Johnson et al., 2006) have quantified PBDE contamination in the lower Columbia River using semipermeable membrane devices (SPMDs). The patterns of PBDE contamination observed in these SPMDs matched those observed in juvenile salmon collected during the same time period. Additionally, anthropogenic wastewater indicators, including some EDCs, were measured in the water column (Lower Columbia River Estuary Partnership, 2007) and in bed sediment (Nilsen et al., 2007).

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In general, a higher proportion of these compounds were detected in the bed sediment than in the water column and at higher concentrations. The connection between these results in the environment (water and sediment) and in salmon is complicated by the migratory nature of salmon.

Passive sampling devices and a combination of chemical analyses and an *in vitro* assay were used in this study to help assess the presence of organic industrial and wastewater compounds (OWCs) entering the Lower Columbia River. The passive samplers integratively sample organic environmental contaminants over prolonged periods concentrating these contaminants considerably over ambient water concentrations making it easier to detect compounds at low levels. Two of the most widely used and studied passive samplers are the SPMD and the polar organic chemical integrative sampler (POCIS). SPMDs consist of a nonporous layflat polyethylene membrane tube containing a neutral lipid (triolein). They are designed to mimic key aspects of the bioconcentration process, which results in elevated contaminant concentrations after exposure to trace hydrophobic organic contaminants (compounds with moderate to high octanol–water partition coefficients [ $K_{ow}$ ] greater than 3) in aquatic environments. The POCIS is designed to mimic an organism's exposure to hydrophilic organic contaminants with low to moderate  $K_{ow}$  (less than 3), and consists of a solid-phase sorbent or mixture of sorbents contained between two sheets of a microporous polyethersulfone (PES) membrane. Sampling of compounds with both of these passive samplers is integrative (*i.e.*, extracted residues are constantly accumulated without significant losses back into the environment) and analyte concentrations are reported as time-weighted average values (Alvarez et al., 2004, 2007; Huckins et al., 2006). These time-weighted average concentrations are important as they provide a measure of exposure to resident fish species which were collected as part of the larger ConHab study (Jenkins et al., 2014–in this issue; Nilsen et al., in this issue-b; Torres et al., in this issue).

## 2. Methods

### 2.1. Study design/site selection

The work described herein contains both a spatial and temporal component covering approximately 86 river miles and three years of field sampling. Initially, nine locations were sampled during the spring and fall of 2008 along the Lower Columbia River starting at Skamania

and ending at Beaver Army Terminal, and one site on the Willamette River at Keizer (Table 1, Fig. 1) to determine the gradient of chemical occurrence under predicted high (spring) and low (fall) flow conditions. The results from this first year reconnaissance study were used to select three sites for more intensive chemical and biological sampling in years 2 and 3. Skamania, with low urban influence, along with Columbia City and Longview, both with moderate to high urban influence, were selected for the intensive studies. Results of the chemical profiles in the water column are discussed in this work. Chemical analyses of the sediments and biota (Nilsen et al., in this issue-b), and the biological measurements (Jenkins et al., 2014–in this issue; Torres et al., in this issue) are reported elsewhere.

### 2.2. Passive samplers

At each study site and deployment period, a single protective canister containing three SPMDs and three POCIS were deployed. Two of the three SPMDs were fortified with performance reference compounds (PRCs) during construction. The PRCs (phenanthrene- $d_{10}$ , pyrene- $d_{10}$ , PCB congeners 14, 29, and 50) are used to adjust uptake kinetics determined in the laboratory for the *in situ* environmental conditions such as flow, temperature, and the buildup of a biofilm on the sampler's surface (Huckins et al., 2006).

### 2.3. Processing and analysis

#### 2.3.1. SPMDs

The SPMDs were processed according to established procedures including dialytic recovery of the sequestered analytes, enrichment/fractionation using size exclusion chromatography (SEC), and fractionation using adsorption chromatography (Alvarez et al., 2008, 2012; Huckins et al., 2006). Specific instrument conditions and calibration techniques for the methods described below are reported elsewhere (Alvarez et al., 2008, 2012). One of the two PRC–SPMDs from each canister and field and laboratory blank were designated for the analysis of organochlorine pesticides (OCs), total PCBs, and select PBDEs (congeners 28, 49, 99, 100, and 153). Following dialysis and SEC fractionation, these samples underwent additional cleanup by passing the extracts through a 5 g gravity-flow Florisil column and then on a 5 g gravity-flow silica gel column generating a PCB fraction and an OC/PBDE fraction. Each fraction from the Silica Gel step was analyzed using a Hewlett-Packard®

**Table 1**

Locations, sampling dates, and precipitation amounts for the study sites in the Lower Columbia River basin.

Site name Coordinates (N, W)	Spring 2008 rainfall (cm)	Fall 2008 rainfall (cm)	Spring 2009 rainfall (cm)	Spring 2010 rainfall (cm)
Willamette River at Keizer 45°02'9", 123°4'13.3"	4/24/08–5/21/08	9/18/08–10/15/08	–	–
Skamania 45°36'52.8", 122°2'28.2"	4/23/08–5/20/08 10.8 cm	9/18/08–10/15/08 11.0 cm	4/8/09–5/4/09 17.2 cm	4/1/10–5/4/10 20.6 cm
Downstream of Government Island 45°36'5.9", 122°36'43.1"	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Downstream of Hayden Island 45°38'27", 122°44'13.9"	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Willamette River at Multnomah Channel 45°37'2.7", 122°47'40.2"	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Mouth of Multnomah Channel 45°50'38.7", 122°48'8.9"	4/21/08–5/19/08	9/16/08–10/14/08	–	–
Columbia City 45°55'11.8", 122°48'44.4"	4/21/08–5/19/08 4.0 cm	9/16/08–10/14/08 5.8 cm	4/7/09–5/6/09 11.6 cm <sup>a</sup>	3/31/10–5/5/10 5.9 cm <sup>a,b</sup>
Between Lewis and Cowlitz 46°3'37", 122°52'56.1"	4/22/08–5/19/08	9/17/08–10/14/08	–	–
Upstream Longview 46°5'23.44", 122°54'47.27"	–	–	–	3/31/10–5/3/10
Longview 46°5'54.9", 122°56'10.8"	4/22/08–5/19/08 2.7 cm	9/17/08–10/14/08 4.2 cm	4/7/09–5/5/09 9.5 cm	3/31/10–5/3/10 12.3 cm
Beaver Army Terminal 46°11'5.6", 123°11'15.1"	4/22/08–5/19/08	9/17/08–10/14/08	–	–

<sup>a</sup> Precipitation amounts for Columbia City during the spring 2009 and spring 2010 periods were not available, therefore levels from the adjacent city, St. Helens, OR, were used.

<sup>b</sup> Daily precipitation amounts for the spring 2010 period at St. Helens, OR were not available for 20 of the 36 days.

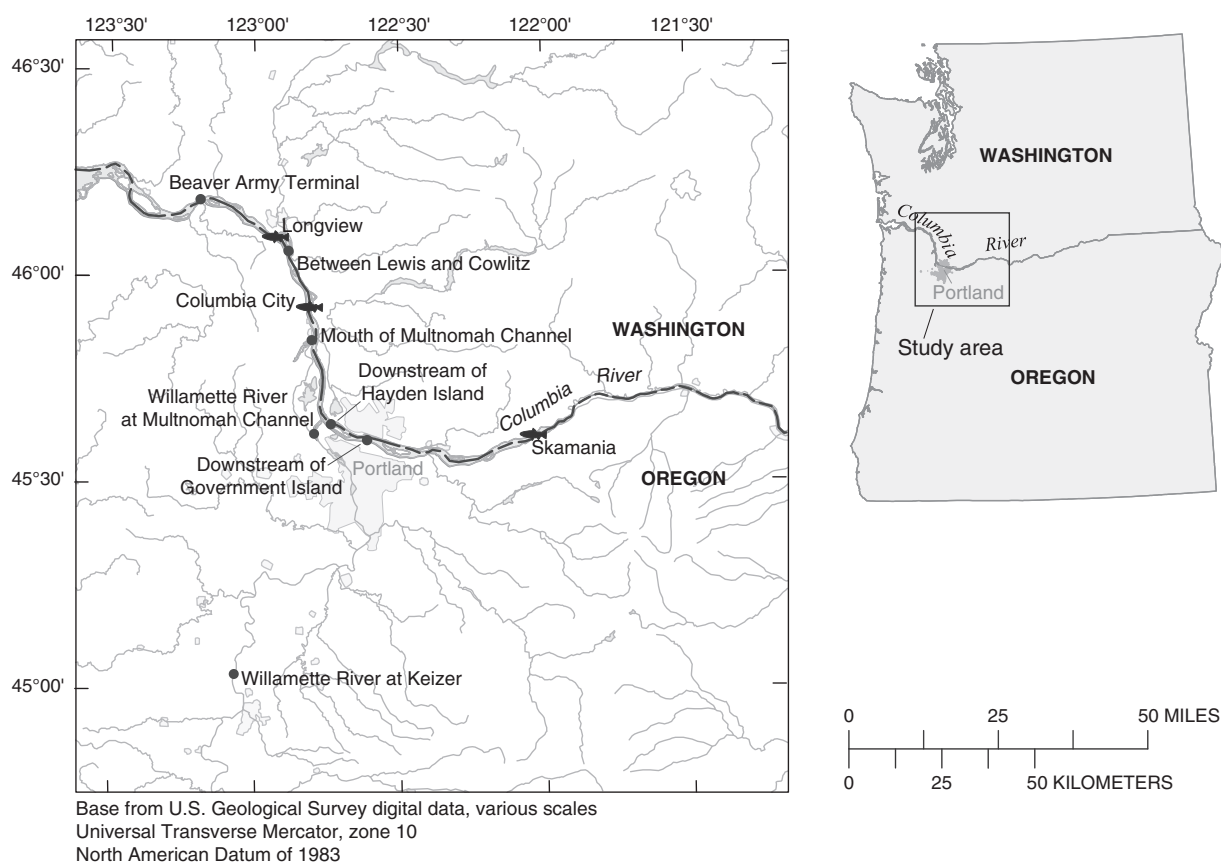


Fig. 1. Locations of the sampling sites for the 2008 to 2010 passive sampler deployments.

5890 series gas chromatograph with an electron capture detector (Hewlett-Packard, Inc., Palo Alto, CA) and a DB-35MS (30 m by 0.25 mm inner diameter by 0.25  $\mu$ m film thickness) capillary column (Agilent Technologies, Inc., Wilmington, DE).

The second PRC–SPMD was designed for the analysis of waste indicator chemicals. Processing of these SPMDs were limited to dialysis followed by SEC due to the diversity of chemical classes included in this chemical group. SPMDs may contain residual methyl oleate from the triolein used in their construction, which can interfere with subsequent GC/MS analyses. To remove the methyl oleate, the SPMD dialysates were fractionated using SEC with a collect window starting at the base of the DEHP calibration peak (used to indicate retention of lipids) and ending just before the sulfur calibration peak (Alvarez, 2010; Lebo et al., 2004). Following SEC, the SPMDs were analyzed using full-scan GC/MS on an Agilent 6890 GC with a 5890 N MSD (Agilent Technologies, Inc., Palo Alto, CA and Wilmington, DE) and a HP5-MS (30 m by 0.25 mm inner diameter by 0.25  $\mu$ m film thickness) capillary column (Agilent Technologies, Inc., Wilmington, DE). The remaining nonPRC–SPMD from each site and blank was archived at  $-20^{\circ}\text{C}$ .

### 2.3.2. POCIS

Two of the three POCIS from each site/blank were designated for analysis of waste indicator chemicals, and the third POCIS was designated for screening of estrogenic chemicals using the Yeast Estrogen Screen (YES). Processing and analysis of the POCIS follow the procedures described by Alvarez et al. (2012). Briefly, each POCIS was opened and the sorbent transferred into a precleaned SPE tube on a vacuum manifold with deionized water. The sorbents were dried by pulling air through for approximately 10 min. Chemicals were extracted from the two waste indicator POCIS using 25 mL of 80:20 (v:v) dichloromethane:methyl-*tert*-butyl ether, after which the two extracts were combined into a single

sample to increase the amount of chemicals present for analysis. The combined extracts were reduced in volume using rotary evaporation and nitrogen blowdown prior to analysis by GC/MSD (Alvarez et al., 2009, 2012).

The POCIS screened by the YES were extracted using 40 mL of methanol and reduced in volume to approximately 1 mL using rotary evaporation. The POCIS for YES were solvent exchanged and diluted to 2 mL with histological-grade alcohol prior to screening. The YES uses a yeast strain transfected with a human estrogen receptor which upon interaction with an estrogen or estrogen-mimic in the presence of a chromophore undergoes a series of reactions resulting in a color change of the test solution (Alvarez et al., 2008, 2012; Rastall et al., 2004). By comparing the color change to a serial dilution of a 17 $\beta$ -estradiol standard, the estradiol equivalents (EEQs) can be calculated as an estimate of the total estrogenicity of chemicals in the sample.

### 2.3.3. Estimation of time-weighted average aqueous concentrations

The estimation of time-weighted average water concentrations of chemicals sequestered by the SPMD and POCIS requires knowledge of the sampling rate for each chemical along with the sampling duration. Using models previously developed (Alvarez et al., 2007; Huckins et al., 2006), data from the analysis of the PRCs added to the SPMDs, and experimentally derived or theoretically estimated sampling rates ( $R_s$ ), the aqueous concentrations of sampled chemicals were estimated.

In SPMDs, the site-specific sampling rate ( $R_{si}$ ) and water concentration ( $C_w$ ) are based on the log  $K_{ow}$  of the chemical, the PRC's rate loss constant ( $k_e$ ), and the SPMD–water partition coefficient ( $K_{sw}$ ). The compound-specific effect ( $\alpha_{(i/PRC)}$ ) on the  $R_s$  due to environmental factors is extrapolated from a third-order polynomial of the log  $K_{ow}$ . The ratio of the compound-specific effects of the target chemical and the PRC multiplied by the PRC  $R_s$  provides the  $R_{si}$  which is used to calculate the  $C_w$ . The models describing the uptake and the use of online

calculators to calculate water concentrations from SPMD data have been discussed in detail (Alvarez, 2010; Huckins et al., 2006). The use of the PRC approach to cover a wide range of chemicals in POCIS has largely failed due to the strong sorptive properties of the adsorbents used in the POCIS (Alvarez et al., 2007). Therefore, estimation of water concentrations from POCIS data requires availability of sampling rates, potentially limiting the number of compounds which can be determined (Alvarez et al., 2007, 2010). This estimation is performed using a simple first-order uptake model for integrative samplers where

$$C_w = \frac{N}{R_s t}$$

$N$  is the concentration of a chemical in the POCIS and  $t$  is the deployment time in days. The list of  $R_s$  values used for the POCIS calculations is given in Table SI-1 of the Supplementary data.

#### 2.4. Quality control

Quality control (QC) measures used in this study included a series of laboratory blanks, field blanks at every site, surrogate recovery spikes of the target chemicals, daily calibration of the instruments, and positive and negative controls for the YES. Method limits of detection (MDL) and of quantification (MQL) were estimated from the average signal-to-noise ratio of the response of targeted chemicals from the instrumental analysis of the laboratory and field matrix blanks (SPMD or POCIS). The MDLs were determined as the mean plus three standard deviations of the response of a coincident peak present in the blanks (Keith, 1991). The MQLs were determined as the mean plus 10 standard deviations of the target chemicals (Keith, 1991). Concentrations which fall between the MDL and MQL have a higher degree of uncertainty and are given for informational purposes only. In cases where no coincident peak was present, the MQL was set at the low-level calibration standard and the MDL was estimated to be 20% of the MQL. This process of determining MDL/MQL values from the blanks accounts for any bias due to the sampler's materials, handling, shipping, storage, and processing.

### 3. Results and discussion

Approximately 100 individual chemicals were analyzed. In order to simplify the presentation of the data and discussion of results, these chemicals were grouped based off their class (chlorinated pesticides) or similar use (OWCs). A list of the individual chemicals and their associated groups are given in Table 2. The group data presented is a summation of the measured concentrations of the individual chemicals in the group. Estimated water concentrations for the individual chemicals are given in Tables SI-2 to SI-4 of the Supplementary data. In this study, trends in contaminant occurrence and concentration were evaluated spatially at all ten sites sampled in 2008 and 2009 as well as temporally at Skamania, Columbia City, and Longview from 2008 to 2010. The lack of replicate data at each of the sampling locations prevented a rugged statistical analysis such as a one-way analysis of variance. For the temporal data, the statistical significance of increasing or decreasing trends in concentration over time was calculated using the Mann–Kendall test (ProUCL version 4.1, US Environmental Protection Agency).

#### 3.1. Spatial trends

In the spring and fall of 2008, nine sites along the lower Columbia River and one on the Willamette River (at Keizer) were sampled in order to determine spatial trends in contaminant profiles. The contaminant profiles followed the predicted trends with fewer numbers of detections and lower concentrations at the rural sites of Skamania and the Willamette River at Keizer to many more detections at higher concentrations in the highly urbanized sites downstream of Portland, Oregon (Tables 3 and 4, and SI-2–SI-4 of the Supplementary data).

**Table 2**  
List of individual target analytes and analyte groups for trend analysis.

Target analyte	Analyte group	Target analyte	Analyte group
cis-Chlordane	∑ Chlordanes	Benzophenone	PCP
cis-Nonachlor	∑ Chlordanes	Camphor	PCP
Heptachlor	∑ Chlordanes	D-Limonene	PCP
Heptachlor Epoxide	∑ Chlordanes	Ethyl citrate	PCP
Oxychlordane	∑ Chlordanes	Menthol	PCP
p,p'-Methoxychlor	∑ Chlordanes	Methyl salicylate	PCP
trans-Chlordane	∑ Chlordanes	Methyl Triclosan	PCP
trans-Nonachlor	∑ Chlordanes	N,N-diethyltoluamide (DEET)	PCP
o,p'-DDD	∑ DDTs	Triclosan	PCP
o,p'-DDE	∑ DDTs	Acetophenone	Fragrance
o,p'-DDT	∑ DDTs	Cashmeran (DPMI)	Fragrance
p,p'-DDD	∑ DDTs	Celestolide (ADBI)	Fragrance
p,p'-DDE	∑ DDTs	Galaxolide (HHCB)	Fragrance
p,p'-DDT	∑ DDTs	Indole	Fragrance
Endosulfan	∑ Endosulfans	Isoquinoline	Fragrance
Endosulfan-II	∑ Endosulfans	Musk Ambrette	Fragrance
Endosulfan Sulfate	∑ Endosulfans	Musk Ketone	Fragrance
cis-Permethrin	∑ Pyrethroids	Musk Xylene	Fragrance
trans-Permethrin	∑ Pyrethroids	Phantolide (AHMI)	Fragrance
Tefluthrin	∑ Pyrethroids	Tonalide (AHTN)	Fragrance
Trifluralin	∑ Pyrethroids	Traseolide (ATII)	Fragrance
alpha-Benzenhexachloride (α-BHC)	∑ Misc OC pesticides	Bisphenol A	Plasticizer
beta-Benzenhexachloride (β-BHC)	∑ Misc OC pesticides	Diethyl phthalate	Plasticizer
Dacthal	∑ Misc OC pesticides	Diethylhexylphthalate (DEHP)	Plasticizer
delta-Benzenhexachloride (δ-BHC)	∑ Misc OC pesticides	N-butyl benzenesulfonamide	Plasticizer
Dieldrin	∑ Misc OC pesticides	4-Octylphenol	Surfactant
Endrin	∑ Misc OC pesticides	p-tert-Octylphenol	Surfactant
Hexachlorobenzene (HCB)	∑ Misc OC pesticides	Tri(2-chloroethyl) phosphate	Alternative FR
Lindane	∑ Misc OC pesticides	Tri(butoxyethyl) phosphate	Alternative FR
Mirex	∑ Misc OC pesticides	Tri(dichloroisopropyl) phosphate	Alternative FR
Pentachloroanisole (PCA)	∑ Misc OC pesticides	Tributyl phosphate	Alternative FR
Chlorpyrifos	Chlorpyrifos	Triphenyl phosphate	Alternative FR
Total PCBs	PCBs	1,4-Dichlorobenzene	Industrial
PBDE congener 28	PBDEs	Anthraquinone	Industrial
PBDE congener 47	PBDEs	Bromoform	Industrial
PBDE congener 99	PBDEs	Isophorone	Industrial
PBDE congener 100	PBDEs	Isopropylbenzene (cumene)	Industrial
PBDE congener 153	PBDEs	para-Cresol	Industrial
1-Methyl naphthalene	PAH	Phenol	Industrial
2,6-Dimethylnaphthalene	PAH	Tetrachloroethylene	Industrial
2-Methyl naphthalene	PAH	Atrazine	Pesticide
Anthracene	PAH	Bromacil	Pesticide
Benzo[a]pyrene	PAH	Carbaryl	Pesticide
Fluoranthene	PAH	Carbazole	Pesticide
Naphthalene	PAH	Chlorpyrifos	Pesticide
Phenanthrene	PAH	Diazinon	Pesticide
Pyrene	PAH	Dichlorvos	Pesticide
Caffeine	Other	Metalaxyl	Pesticide
Cotinine	Other	Prometon	Pesticide

Chemical groups with the highest concentrations in the spring and fall of 2008 were the PAHs (0.29–79 ng/L), plasticizers (below detection–890 ng/L), pesticides (below detection–260 ng/L), and industrial chemicals (below detection–120 ng/L). The highest concentrations of these chemicals were localized between the Downstream of Hayden Island site and the Longview site downstream of Portland, Oregon. In the spring of 2008, the total estrogenicity of chemical sampled increased with increasing distance downstream of Skamania, reaching a maximum at the Columbia City site where inputs from wastewater treatment plants



**Table 3**

Cumulative amounts of waste indicator chemicals measured at each site over four sampling periods.

	Willamette River at Keizer	Skamania	Downstream of Government Island	Downstream of Hayden Island	Willamette River at Multnomah Channel	Mouth of Multnomah Channel	Columbia City	Between Lewis and Cowlitz	Upstream Longview	Longview	Beaver Army Terminal
	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
<i>Spring 2008</i>											
∑ PAHs	7.0	6.2	5.9	0.29	11	29	79	11	----	73	9.8
∑ Industrial	22	14	18	ND	10	41	58	13	----	100	18
∑ PCPs	ND	ND	18	12	2.6	12	38	ND	----	ND	13
∑ Fragrances	12	ND	4.5	4.0	23	12	15	ND	----	7.0	3.9
∑ Pesticides	ND	0.45	0.50	ND	170	130	260	0.38	----	3.5	0.35
∑ Alt FR	ND	ND	0.27	ND	ND	ND	3.6	ND	----	ND	ND
∑ Plasticizers	30	31	140	63	63	58	77	35	----	11	51
∑ Other	ND	ND	2.9	ND	16	ND	ND	ND	----	ND	ND
EEQ	1.5	0.16	0.11	0.67	0.75	0.77	1.2	0.21	----	0.30	0.26
<i>Fall 2008</i>											
∑ PAHs	4.4	2.2	1.7	2.3	20	7.2	16	11	----	7.6	5.2
∑ Industrial	17	ND	20	ND	15	33	ND	ND	----	120	80
∑ PCPs	ND	ND	ND	ND	ND	ND	ND	21	----	1.2	ND
∑ Fragrances	7.7	ND	3.5	6.1	5.1	ND	17	ND	----	7.1	0.15
∑ Pesticides	0.41	ND	ND	ND	ND	ND	ND	ND	----	ND	ND
∑ Alt FR	ND	ND	ND	ND	ND	ND	ND	ND	----	ND	ND
∑ Plasticizers	280	ND	77	260	310	890	220	170	----	140	130
∑ Other	ND	ND	ND	ND	ND	ND	ND	ND	----	ND	ND
EEQ	1.2	2.5	0.24	0.31	1.2	0.82	0.66	0.24	----	2.2	3.4
<i>Spring 2009</i>											
∑ PAHs	----	4.0	----	----	----	----	7.9	----	----	14	----
∑ Industrial	----	ND	----	----	----	----	ND	----	----	1.5	----
∑ PCPs	----	ND	----	----	----	----	ND	----	----	ND	----
∑ Fragrances	----	ND	----	----	----	----	16	----	----	59	----
∑ Pesticides	----	3.3	----	----	----	----	1.3	----	----	ND	----
∑ Alt FR	----	ND	----	----	----	----	ND	----	----	ND	----
∑ Plasticizers	----	270	----	----	----	----	460	----	----	520	----
∑ Other	----	ND	----	----	----	----	ND	----	----	ND	----
EEQ	----	ND	----	----	----	----	0.21	----	----	0.08	----
<i>Spring 2010</i>											
∑ PAHs	----	0.77	----	----	----	----	0.66	----	0.74	0.54	----
∑ Industrial	----	0.20	----	----	----	----	ND	----	ND	ND	----
∑ PCPs	----	2.1	----	----	----	----	1.1	----	0.78	ND	----
∑ Fragrances	----	1.3	----	----	----	----	1.0	----	1.1	0.45	----
∑ Pesticides	----	0.008	----	----	----	----	3.4	----	0.071	ND	----
∑ Alt FR	----	ND	----	----	----	----	1.7	----	0.95	1.6	----
∑ Plasticizers	----	17	----	----	----	----	24	----	ND	ND	----
∑ Other	----	ND	----	----	----	----	ND	----	ND	ND	----
EEQ	----	ND	----	----	----	----	0.10	----	0.74	0.09	----

PAHs: polycyclic aromatic hydrocarbons.

PCPs: personal care products.

Alt FR: alternative flame retardants, phosphate-based.

EEQ: Estimated estradiol equivalents, total estrogenicity measured by the yeast estrogen screen.

ND: not detected.

----: site not sampled during this period.

(WWTPs) are more frequent. This trend was not retained in the fall of 2008 where the EEQ results were considerably more variable. Halogenated chemicals such as PCBs, PBDEs, chlordanes, and endosulfans were also detected at all sites, but at concentrations one to two orders of magnitude lower.

The chemicals and measured concentrations from this work are in general agreement with observations from other published studies. McCarthy and Gale (2001) reported lower concentrations of PCBs and similar concentrations of chlorinated pesticides and PAHs at several sites between Skamania and Beaver Army Terminal sampled using SPMDs in 1997 and 1998. In April of 2005, SPMDs deployed at Beaver Army Terminal detected PCBs and PBDEs (Lower Columbia River Estuary Partnership, 2007). In this work, water concentrations were not calculated; therefore, a comparison of the data other than detections was not possible. Chlorinated pesticides and PAHs were not detected in the 2005 study; however, their reported detection limits, which were 10 to 400 times greater than in the present study, would have prevented detection of most of these chemicals. Sandvik and Seiders (2012) also

used SPMDs to sample PCBs, PBDEs, chlorinated pesticides, and PAHs at Beaver Army Terminal in April to May of 2010 and May to June of 2011. Similar chemicals were detected in the Sandvik and Seiders (2012) work and that of the present study, with estimated water concentrations of the two studies generally within a factor of 2 or 3 of each other.

In 2009, effluents from WWTPs and stormwater runoff samples were collected from several sites along the Columbia River including Longview and St. Helens, which is approximately 4 river miles upstream of the Columbia City site (Morace, 2012). In these samples, a variety of OWCs were detected, including surfactants, phosphate flame retardants, personal care products (PCPs), fragrances, plasticizers, and sterols, similar to the findings from the present study. In a separate part of the ConHab project, sediment samples were collected and analyzed from each of these selected sites in 2010 (Counihan et al., 2014—in this issue). The sediment-focused portion of the study revealed the similar trend as the water measurements with higher concentrations of industrial compounds, PCPs and PAHs, compared to lower

**Table 4**

Cumulative amounts of legacy organic contaminants measured at each site over four sampling periods.

	Willamette River at Keizer	Skamania	Downstream of Government Island	Downstream of Hayden Island	Willamette River at Multnomah Channel	Mouth of Multnomah Channel	Columbia City	Between Lewis and Cowlitz	Upstream Longview	Longview	Beaver Army Terminal
	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
<i>Spring 2008</i>											
∑ PBDEs	0.17	0.040	0.066	0.122	0.24	0.24	0.35	0.049	–	0.17	0.062
∑ PCBs	ND	ND	3.4	3.9	2.8	0.54	2.1	1.2	–	1.2	0.94
∑ DDTs	0.077	0.19	0.66	0.77	0.43	0.56	0.50	0.23	–	0.38	0.21
∑ Chlordanes	0.021	0.019	0.042	0.12	0.057	0.16	0.17	0.016	–	0.053	0.024
∑ Pyrethroids	0.055	0.057	0.17	0.006	0.006	0.094	0.17	0.034	–	0.18	0.050
∑ Endosulfans	1.2	1.1	1.0	2.3	1.4	1.3	0.99	0.80	–	0.75	0.76
∑ Misc OC pest	0.31	0.16	0.27	0.30	0.52	0.55	0.67	0.18	–	0.29	0.17
Chlorpyrifos	0.093	0.21	0.36	0.48	0.28	0.52	0.30	0.28	–	0.29	0.30
<i>Fall 2008</i>											
∑ PBDEs	0.45	0.019	0.046	0.12	0.14	0.068	0.081	0.024	–	0.049	0.054
∑ PCBs	ND	0.47	ND	0.84	1.3	3.7	4.7	0.69	–	0.93	0.53
∑ DDTs	0.12	0.17	0.16	0.16	0.32	0.18	0.23	0.072	–	0.11	0.18
∑ Chlordanes	0.064	0.018	0.038	0.026	0.078	0.055	0.067	0.011	–	0.027	0.029
∑ Pyrethroids	0.10	0.022	ND	0.030	0.031	0.015	0.10	0.046	–	0.038	0.027
∑ Endosulfans	0.15	0.26	0.70	0.35	0.55	0.25	0.20	0.28	–	0.28	0.37
∑ Misc OC pest	0.41	0.068	0.10	0.072	0.19	0.092	0.18	0.054	–	0.11	0.14
Chlorpyrifos	0.083	0.010	0.034	0.015	0.047	0.023	0.048	0.013	–	0.035	0.026
<i>Spring 2009</i>											
∑ PBDEs	–	0.013	–	–	–	–	ND	–	–	ND	–
∑ PCBs	–	ND	–	–	–	–	1.0	–	–	5.2	–
∑ DDTs	–	0.11	–	–	–	–	0.066	–	–	0.060	–
∑ Chlordanes	–	0.077	–	–	–	–	0.014	–	–	0.12	–
∑ Pyrethroids	–	ND	–	–	–	–	ND	–	–	ND	–
∑ Endosulfans	–	1.8	–	–	–	–	0.62	–	–	0.34	–
∑ Misc OC pest	–	0.046	–	–	–	–	0.10	–	–	0.070	–
Chlorpyrifos	–	0.14	–	–	–	–	0.15	–	–	0.093	–
<i>Spring 2010</i>											
∑ PBDEs	–	1.1	–	–	–	–	ND	–	0.34	0.41	–
∑ PCBs	–	1.0	–	–	–	–	0.21	–	0.27	0.27	–
∑ DDTs	–	0.58	–	–	–	–	0.14	–	0.12	0.11	–
∑ Chlordanes	–	0.22	–	–	–	–	0.013	–	0.008	0.007	–
∑ Pyrethroids	–	0.47	–	–	–	–	ND	–	ND	ND	–
∑ Endosulfans	–	1.7	–	–	–	–	1.9	–	1.3	0.56	–
∑ Misc OC pest	–	0.26	–	–	–	–	0.16	–	0.083	0.21	–
Chlorpyrifos	–	0.24	–	–	–	–	0.51	–	0.82	0.53	–

concentrations of flame retardants and chlorinated compounds in sediments.

### 3.2. Temporal trends

Using the spatial data from the 2008 sampling events and osprey egg data (Henny et al., 2011) which was used to provide a linkage to the biomagnification of PBDEs through the food chain, three sites were selected for additional sampling to assess temporal trends in contaminant profiles and for the rigorous biological sampling reported in this special issue (Jenkins et al., 2014–in this issue; Nilsen et al., 2014–in this issue-b; Torres et al., in this issue). Skamania, the farthest upstream site at river mile 140, was selected due to the presence of few target chemicals at relatively low concentrations. Skamania is located downstream of Bonneville Dam in a largely forested area with no known point sources of contaminants. The Columbia City site, at river mile 82, and the Longview site, at river mile 66, are in highly urbanized regions downstream of Portland, Oregon. The presence of contaminants at the Columbia City site is influenced by inputs from the Multnomah Channel, stormwater runoff, and a WWTP at nearby St. Helens, Oregon. The Longview site is near the Port of Longview, which is a deep-water port with both domestic and international shipping traffic. Two WWTPs near Longview also discharge in the vicinity of the sampling site provides additional information on these sites.

Streamflow is an important environmental factor that could affect temporal trends in chemical concentrations in the river, assuming

constant seasonal input. Correlations to flow could not be made as the only data available was from a stream gauge at Beaver Army Terminal at river mile 54. The flow conditions at this site were not expected to be representative of the three temporal sites due to the inputs of several tributaries along this stretch of river, especially Skamania nearly 90 river miles upstream. Instead, precipitation, in the form of rainfall amounts, was used as a measure of potential surface runoff and dilution in the river. The spring sampling periods coincided with the end of the heavy winter rainy season. During each of the sampling periods, Skamania received approximately twice the rainfall as Columbia City and Longview (Table 1, Fig. 2). Precipitation records for Columbia City in 2009 and 2010 were not available; therefore, data from adjacent city of St. Helens, OR, was used. The rainfall amount for St. Helens in 2010 is incomplete as the records were missing data for 20 of the 36 days; however, based on the three previous sampling periods, the rainfall amount at Columbia City should be similar to that of Longview. The amount of rainfall increased 1.9-fold at Skamania, 2.9-fold at Columbia City, and 4.6-fold at Longview from the spring 2008 sampling to the spring 2010 sampling (Table 1, Fig. 2).

For the OWCs, the PAHs, industrial chemicals, and PCPs exhibited the greatest change in concentrations over time (Table 3, Fig. 2). The industrial chemicals, dominated by anthraquinone and tetrachloroethylene, had the greatest change in concentrations over time ranging from 120 ng/L at Longview in fall 2008 to not detected in spring 2010 (Table 3, Fig. 2). PAH concentrations also decreased with increasing precipitation, but to a much smaller degree, potentially suggesting that

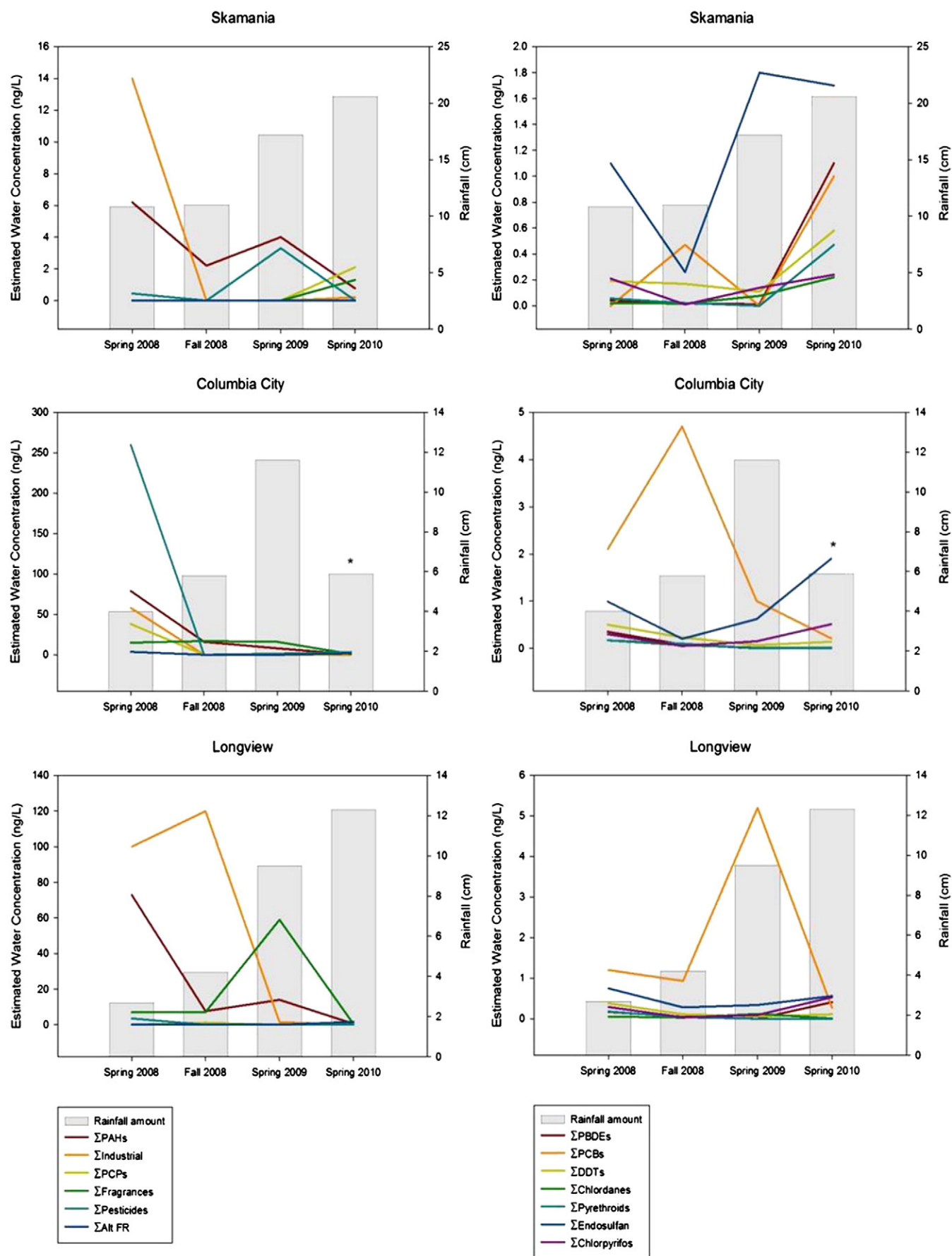


Fig. 2. Cumulative concentrations of chemicals compared to rainfall amounts measured at the primary study sites over four sampling periods. "\*" Precipitation data was only available for 16 of the 36 days the passive samplers were deployed.

surface runoff was contributing to the PAH loading into the river. Personal care products, largely benzophenone in the spring 2008 sample, were detected at Columbia City only, ranging from 38 ng/L (total) to not detected. Columbia City also was the site of the greatest change in pesticide (atrazine) concentrations over time, ranging from 260 ng/L in spring 2008 to not detected. Total estrogenicity measured by the YES also showed the trend of decreasing concentrations over time. Even with the seemingly large concentration differences between temporal samples for particular chemicals, few exhibited a statistically significant trend of increasing or decreasing concentrations, as concentrations were variable in most cases. The Mann–Kendall test for trends determined only the total PAHs at Skamania and the total PAHs, total Chlordanes, and the EEQ at Columbia City had statistically significant evidence of a decreasing trend at the 95% confidence interval.

The trend of decreasing water concentrations of OWCs with increasing river flow has been reported previously. Kolpin et al. (2004) reported decreasing concentrations of OWCs as stream flow increased, largely as a result of dilution. Similarly, Villa et al. (2012) observed increased concentrations in the Molgora River, Italy, during periods of the year where the river flows were reduced. Alvarez et al. (2009) did not observe seasonal differences in OWC concentrations in a WWTP effluent study; however, the ratio of WWTP effluent to mean stream flow remained largely unchanged between sampling periods therefore effects of dilution may not have been observed.

The opposite trend was observed for some of the legacy (PCBs and organochlorine pesticides) contaminants where average water concentrations increased with increasing precipitation in 2009 and 2010. Differences in the water concentrations of the legacy contaminants over time were variable; however, slight increases were observed in 2010. Endosulfan showed the greatest increase at Skamania and Columbia City over time. Endosulfan is a popular pesticide used on Christmas trees, timber, fruit and ornamental trees, and several types of vegetables. The State of Oregon banned the use of endosulfan after July 31, 2012 (Oregon Department of Agriculture, 2012). Although most of the other legacy contaminants measured have been banned for decades, their presence in the environment continues to be a problem. Due to their hydrophobic character, these contaminants are largely associated with sediments, particulate matter, and biota in the environment. With increased precipitation, higher loadings of contaminant-laden particles enter the river *via* surface runoff and resuspension of bed sediments. This results in increased water concentrations as resolubilization of a fraction of the sorbed chemicals occurs. Sun et al. (2006) reported that precipitation, in the form of both rain and snow, is an important transport mechanism for chlorinated pesticides to enter the aquatic environment.

Carlson et al. (2004) and Sun et al. (2006) found higher concentrations of banned pesticides (chlordanes, DDTs) in Great Lakes precipitation during periods with snow, which “scrubs” particulate-bound chemicals out of the atmosphere. Snowmelt from the Cascade Range could also contribute to the loading of the legacy contaminants into the Columbia River; however, this impact is expected to be minor, as snowmelt would most directly impact regions upstream of our study region, where flows are regulated by the numerous dams and reservoirs upstream of Bonneville Dam (Fuhrer et al., 1996). Also, the peak contributions to flow from snowmelt generally occur from May through June, which was at the end of the deployment of the passive samplers (Fuhrer et al., 1996). It would be expected that the potential impact of snowmelt as a contaminant source would be most prominent at Skamania (the uppermost site), which did have elevated levels of PCBs, DDTs, and chlordanes compared to many of the downstream sites (Table 4). It is likely that these levels due to the snowmelt were attenuated farther downstream and replaced by more localized point sources.

#### 4. Conclusions

This work represents the largest analyte list sampled by passive samplers in a multi-location/multi-year study. The spatial and temporal

profiles of different organic contaminants throughout the Lower Columbia River were determined for the period of 2008 to 2010. Spatial trends followed expected patterns with fewer contaminants detected at lower concentrations in the rural sampling sites and the highest numbers of detections of contaminants and concentrations at the urban sites. Temporal trends were more difficult to determine; however, different trends were suggested for different types of chemicals. Concentrations of OWCs tended to decrease with increased rainfall, likely the result of dilution, whereas concentrations of legacy contaminants slightly increased with increased rainfall suspected to be the result of atmospheric deposition and resuspension of contaminated bed sediments. However, sampling over much longer periods would be necessary to fully determine contaminant trends.

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Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.07.128>.

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